



PATENT SPECIFICATION 573,384

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COMPLETE SPECIFICATION

Preparation of Hydracrylic Acid

We, AMERICAN CYANAMID COMPANY, a corporation organized under the laws of the State of Maine, United States of America, of 30 Rockefeller Plaza, New York, New York, United States of America, (assignees of GEORGE ROBERT GRIFFIN and BRYAN COLLINS REDMON, both citizens of the United States of America, of Catoona Lane, Stamford, Connecticut, United States of America, and 70 Strawberry Hill Avenue, formerly of Stamford, Connecticut, respectively), do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the production of hydracrylic acid.

An object of this invention is to prepare hydracrylic acid in high yields.

This and other objects are attained by converting sodium hydracrylate, potassium hydracrylate or calcium hydracrylate to hydracrylic acid by means of the stoichiometrical quantity of a strong acid, e.g. sulphuric acid, and by carrying out the reaction at a relatively low temperature namely between about 30°—50° C.

The following example, in which the proportions are in parts by weight, is given by way of illustration and not in limitation.

EXAMPLE.

Ethylene cyanohydrin	-	710	parts
Sodium hydroxide	-	404	"
Water	-	1000	"
Sulphuric acid (95.5%)	-	518	"

The ethylene cyanohydrin is added to a solution of the sodium hydroxide in the water slowly and either continuously or in small proportions over a period of about 1 hour. The reacting mixture is maintained at a temperature of about 95°—100° C. during the addition of the ethylene cyanohydrin and it is agitated by any convenient method.

A large proportion of the ammonia which is liberated during the addition of the ethylene cyanohydrin is given off and its removal may be facilitated by introducing a small stream of steam or air into

the reacting mixture. After all of the ethylene cyanohydrin is added, the solution may be maintained at the reaction temperature for from a few minutes to an hour or more in order to insure the complete hydrolysis of any unreacted ethylene cyanohydrin. The residual ammonia may be volatilised from the solution and part of the water may be removed, thereby providing a solution of sodium hydracrylate of about 95—100% purity. The solution may be advantageously evaporated to the point where solid material begins to precipitate from the hot solution. It is desirable that the ammonia set free by the hydrolysis of the ethylene cyanohydrin be completely removed. It is then possible to compute with a high degree of certainty the stoichiometrical quantity of acid to react with the sodium hydracrylate. On the other hand, if ammonia be present an analysis is necessary since the ammonia must be neutralized and therefore sufficient acid must be added to convert the sodium hydracrylate to hydracrylic acid and also to neutralize the ammonia.

The solution of sodium hydracrylate prepared in accordance with the foregoing description is cooled to about 40° C. after which the sulphuric acid is added. During the addition of the acid the temperature of the solution is maintained at about 30°—50° C. Substantially all water is then removed from the solution by heating under absolute pressure of about 30 mm. of mercury and with constant evaporation. A small proportion of an extracting solvent, e.g. ethanol, acetone, etc., may be mixed with the resulting slurry and the sodium sulphate filtered from the hydracrylic acid and extraction solvent. The sodium sulphate filter cake is extracted continuously or by decantation with the extraction solvent. The filtrate and the extraction solvent are combined and filtered to remove any residual sodium sulphate. The extraction solvent is removed from the combined solution by evaporation at atmospheric pressure followed by evaporation at about 20—30 mm. of mercury absolute pressure. The product is substantially pure hydracrylic acid.

crylic acid and it is an amber coloured viscous liquid. A yield of about 95% of the theoretical is obtained.

In place of the solution of sodium hydracrylate prepared in the first part of the preceding example, we may substitute an aqueous solution of sodium potassium or calcium hydracrylate which is prepared by dissolving the salt obtained from any source in water.

If the amount of sodium hydracrylate in solution is not accurately known the solution should be analyzed in order to determine the stoichiometrical equivalent of sulphuric acid which is to be added.

The hydracrylic acid may be separated from the sodium sulphate or other metal salt resulting from the decomposition of the hydracrylic acid salt and acid which is added, by any suitable extracting solvent or by means of centrifuging or any other desired means.

The sulphuric acid is added in the stoichiometrical proportions required for conversion of the sodium hydracrylate to the hydracrylic acid. This is necessary because the separation of hydracrylic acid and sulphuric acid is extremely difficult and not commercially feasible. Similarly, the use of less than the stoichiometrical quantity of sulphuric acid gives a reduced yield, inasmuch as all of the sodium hydracrylate will not be converted to hydracrylic acid and, furthermore, difficulties are encountered in separating sodium hydracrylate from the hydracrylic acid.

The temperature of the reaction mixture during the conversion of the sodium hydracrylate to hydracrylic acid should not be permitted to rise above about 50° C. since at higher temperatures the hydracrylic acid is dehydrated to acrylic acid, thereby reducing the yield of product. Temperatures above about 30° C. are preferably employed because the character of the precipitated salt is such that it is easier to filter. This is probably because the sodium sulphate decahydrate is largely produced at low temperatures. Since the reaction of the sulphuric acid with sodium hydracrylate is an exothermic reaction, the sulphuric acid should be added at such a rate that the temperature does not rise above the critical point of about 50° C.

Potassium or calcium hydracrylate may also be converted to the acid in accordance with our process. Such salts may be prepared as an initial step in the process by reaction of ethylene cyanohydrin with an aqueous solution of a strong base of potassium or calcium as indicated in the foregoing example and the resulting solution is treated with a strong acid in

accordance with the process described and claimed herein, to produce free hydracrylic acid. The reaction of ethylene cyanohydrin with the alkaline material is preferably carried out by adding ethylene cyanohydrin to an aqueous solution of the alkaline material which is maintained at about 70°—100° C. and desirably at about 100° C. This process is described and claimed in our copending Application Number 15933, filed 28th September, 1943.

Any of the strong mineral acids are suitable for conversion of the hydracrylate salts into hydracrylic acid, e.g. sulphuric acid, hydrochloric acid, nitric acid (diluted in order to avoid nitration and oxidation), phosphoric acid, as well as organic acids stronger than hydracrylic acid, such as chloroacetic acid (mono-, di- and tri-), maleic, oxalic acid, etc.

Hydracrylic acid is useful in the preparation of acrylic acid and its esters, as well as for the production of many other organic compounds. The hydracrylic acid esters have a wide field of application as solvents in coating compositions, as plasticizers and for many other purposes.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. In a process for preparing hydracrylic acid, the step which comprises treating sodium hydracrylate, potassium hydracrylate or calcium hydracrylate with an acid stronger than hydracrylic acid in an aqueous solution maintained at a temperature between 30° C. and about 50° C., the proportion of acid stronger than hydracrylic acid being substantially stoichiometrically equivalent to the amount of the hydracrylate.

2. In a process for preparing hydracrylic acid, the step which comprises treating sodium hydracrylate, potassium hydracrylate or calcium hydracrylate with a strong mineral acid in an aqueous solution maintained at a temperature between about 30° C. and about 50° C., the relative proportions of said hydracrylate and the mineral acid being substantially stoichiometrically equivalent.

3. In a process of preparing hydracrylic acid, the step which comprises treating sodium hydracrylate with sulphuric acid in an aqueous solution maintained at a temperature of about 30° C.—50° C., the proportions of sodium hydracrylate and of sulphuric acid being substantially stoichiometrically equivalent.

4. A process for preparing hydracrylic acid which comprises adding ethylene cyanohydrin to an aqueous solution of a strong base of metal selected from the
- 5 group consisting of sodium potassium or calcium at a temperature of about 70° C.—100° C., completely removing NH₃, adding to the resulting solution an acid stronger than hydracrylic acid in an
- 10 amount stoichiometrically equivalent to the salt of hydracrylic acid present in the solution, maintaining the temperature of said solution during the addition of said acid between about 30° C. and about
- 15 50° C. and separating the hydracrylic acid thus produced.
5. In a process of preparing hydracrylic acid, the steps which comprise adding ethylene cyanohydrin to an aqueous solution of sodium hydroxide at a temperature of about 70° C.—100° C., completely removing NH₃, adding an amount of sulphuric acid equivalent to the sodium hydracrylate thus produced to the resulting solution and maintaining said sodium at a temperature of about 30° C.—50° C. during the addition of the acid.

Dated this 28th day of September, 1943.
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